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Communication

Innovative Process for Strategic Metal Recovery from Electric Arc Furnace Slag by Alkaline Leaching

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Abstract: Currently, Electric Arc Furnace Slag (EAFS) is undervalued and is therefore only used in road construction, while blast furnace slag (BFS) is used as an interesting alternative in construction materials to replace natural aggregates in the manufacture of concrete. Steel slag (SS) represents a promising secondary resource due to its high content of critical metals, such as chromium (Cr) and vanadium (V). These metals are essential for various strategic industries, making it crucial to consider slag as a resource rather than waste. However, the primary challenge lies in selectively recovering these valuable metals. In this work, we explore the development of a hydrometallurgical process aimed at efficiently extracting Cr and V from Electric Arc Furnace Slag (EAFS). The characterization of the investigated EAFS shows that the main crystalline phases contained in this heterogeneous material are srebrodolskite, larnite, hematite, and spinel such as probably magnesio-chromite. The targeted metals seem to be dispersed in various mineral species contained in the SS. An innovative hydrometallurgical method has been explored, involving physical preparation by co-grinding slag with alkaline reagents followed by treatment in a microwave furnace to modify the metal-bearing species to facilitate metal processing dissolution. The results obtained showed that the leaching rates of Cr and V were, respectively, 100% and 65% after 15 min of treatment in the microwave furnace, while, after 2 h of conventional heat treatment, as explored in a previous study, 98% and 63% of the Cr and V were, respectively, leached.



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Keywords: slags; strategic metals; recovery; microwaves; alkaline reagents; leaching

1. Introduction

The generic term steel slag (SS) encompasses several materials with different physico-chemical characteristics. These are artificial mineral matrices, classified as waste produced in very large quantities (several million tons per year in France) simultaneously with cast iron or steel in liquid form at temperatures close to 1500 °C by the steel industry. They are particularly rich in strategic metals [1]. These materials are nevertheless mostly stored in a “slag heap” in the steel industry and constitute a potential impact on the environment and public health. Long considered waste from steel manufacturing, iron and steel slag are today recognized as truly precious and valuable materials. Historically, steelmakers disposed of these materials by storing them in landfills near production sites. The progressive awareness of the intrinsic quality of these materials (and therefore of their market values) has allowed for the emergence of organized value chains since 1930 [2]. Contrarily to their previous status as waste, slag is basically valorized as by-products of steel and cast iron manufacturing and used in road or construction applications, for example. The fields of application are, today, diverse and varied. Blast slag can be safely used along with clinker and gypsum for the production of cement, in the preparation of materials such as ceramic glass, silica gel, ceramic tiles, bricks, etc. LD slag can be used in soil conditioners, fertilizers, the recovery of metal values, etc. EAF oxidizing slag is used as a concrete aggregate. Steel slag is also used in road and hydraulic construction [3–5].

Because of the scarcity of raw materials and increasingly drastic environmental laws, industries have been forced to create more efficient and sustainable models of socio-economic development. The recovery of certain wastes and co-products such as steel slag has become a solution to limit the storage of these materials. Each slag is considered a unique product because it comes from the manufacture of a specific type of steel [6,7]. Currently, Electric Arc Furnace Slag (EAFS) is poorly valorized and is mainly used in road construction, while blast furnace slag (BFS) could be used as an interesting alternative in building materials to replace natural aggregates in concrete manufacturing, for example [8]. Slags could be a very good secondary resource, as they contain large amounts of different metals such as chromium, vanadium etc. Therefore, they should be considered as a resource, not as waste. The challenge is to be able to selectively recover the strategic metals (Cr and V) they contain. There is a wide variety of hydrometallurgical processes described in the literature depending on the nature of the metal to be extracted, the composition of the gangue, or even the extraction context chosen according to the physicochemical conditions of the environment (temperature, pressure, pH, etc.). X. Wang et al. [9] developed a process to separate and recover vanadium and chromium from V-Cr-bearing reducing slag. The investigated process included four procedures: low-temperature sulfate roasting, reduction leaching, selective oxidation, and preparation, by, respectively, calcination or precipitation of vanadium and chromium oxides. They were able to obtain Cr and V leaching efficiencies reaching 99.7% and 99.6%, respectively, by sulphating roasting at low temperature and leaching reduction. The products of V_2O_5 with purity of 99.1% and Cr_2O_3 with purity of 98.9% were obtained by treating ammonium poly-vanadate and Cr^{III} precipitate, respectively.

The steel industries are working to develop new alternatives to valorize these slags in order to achieve a double objective: the preservation of natural virgin material resources and a reduction in slag treatment and storage costs. In this work, the development of an EAFS hydrometallurgical process to recover strategic metals by microwave-assisted leaching is considered. This method allows for the rapid heating of slag and alkaline reagent mixtures to improve the kinetics of the extraction of the valuable metals contained in them and reduce the environmental impact [10,11]. Moreover, such a process is known to allow for the formation of highly reactive entities named radicals, which induce high reaction kinetics. This process is established in order to study the operating parameters and conditions favoring thermal treatment as well as the leaching of metals. Among all the contained elements, this study was specifically focused on chromium and vanadium due to their respective contents in the targeted slag and the increasingly strong industrial demand inducing an increase in their value.

Kokko M. et al. [12] developed an innovative two-stage direct leaching process for selectively recovering calcium (Ca) and vanadium (V) from Electric Arc Furnace (EAF) Slag, which is obtained after furnace hydrogen direct reduction of iron process (HRI). The process is designed to optimize the recovery of these valuable elements through selective leaching in different stages using specific chemical solutions. For the first stage, the leaching of calcium (Ca) and magnesium (Mg), they used a mixture of nitric acid, ammonium nitrate, and water ($HNO_3-NH_4NO_3-H_2O$) to leach calcium and magnesium selectively. This solution works efficiently to extract these alkaline earth metals, as they are more readily soluble in the acidic environment provided by nitric acid, while other elements in the slag remain mostly unaffected. For the second stage: the leaching of vanadium (V), two different solutions were used to extract vanadium, as follows.

1. **Sodium carbonate and sodium hydroxide in water ($Na_2CO_3-NaOH-H_2O$):** This solution creates an alkaline medium that facilitates the selective dissolution of vanadium, particularly vanadium in its higher oxidation states, as vanadium compounds tend to form soluble complexes in alkaline conditions.
2. **Ammonium carbonate in water ($(NH_4)_2CO_3-H_2O$):** Ammonium carbonate also creates an alkaline environment but offers a slightly different chemical interaction, which

can further aid in vanadium dissolution, depending on the slag's composition and the specific vanadium phases present.

This two-stage process effectively separates calcium and magnesium from vanadium, minimizing cross-contamination between the elements and enhancing the purity of the recovered materials. This approach represents an efficient method for the valorization of EAF slag, reducing waste and recovering valuable resources, particularly in processes where furnace hydrogen reduction of iron is utilized.

Mantang Ding [13] proposed that submerged arc furnace carbothermic reduction method, sub-molten salt method, vanadium alloy production, acid roasting–leaching calcification and two-part acidification to extract vanadium are areas for future development.

2. Materials and Methods

A representative sample of Electric Arc Furnace Slag (EAFS) was provided by a French steel company. Due to its high content of metals, this slag cannot be used in road construction or the cement industry without pretreatment. This slag was generated using the EAF process and sampled after extracting the iron scrap by low-intensity dry magnetic separation. First, the representative slag sample was characterized to adapt its preparation pathway before the implementation of chemical modification of metal-bearing species and the leaching process. Since the EAFS sample is heterogeneous, an appropriate sampling method is crucial to ensure that the samples used for this study accurately represent the entire slag batch. Heterogeneity in slag can arise from variations in the particle size, metal content, and mineral composition, which can affect data consistency if not properly accounted for. The protocol consists of size reduction using crushing, grinding, and then sieving steps to obtain a particle size less than 125 μm , while minimizing the overproduction of fine particles, to obtain a homogenous and representative powder. After the grinding and sampling steps, fine characterization was carried out on a sample with a smaller than 125 μm particle size using conventional analytical techniques. The results of the chemical analysis were obtained by using Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (Agilent 7800, Agilent Technologies, Santa Clara, CA, USA). X-ray Diffraction (XRD) measurements were performed at room temperature using a BRUKER D8 Advance $\theta/2\theta$ diffractometer equipped (BRUKER, Billerica, MA, USA) with a Lynxeye energy dispersive one-dimensional detector (Cu-K α radiation, 40 kV and 40 mA; 2θ from 10° to 80° with a step of 0.02° and counting time of 0.5 s per step) This technique allows for crystalline phase identification, completed through the determination of the chemical element distribution through Scanning Electron Microscopy and Energy Dispersion Spectroscopy (FE-SEM, Tescan MIRA3, Brno, Czech Republic) (SEM-EDS) mapping, performed on a polished representative sample.

The representative samples of EAFS were then mixed and co-grinded for 15 min with different alkaline reagents by taking a slag-versus-reagent-weight ratio equal to 1. Regarding the preliminary chemical modification of the EAFS sample, various parameters have been optimized, including the nature of the alkaline reagents and the volume of water added (1 mL) before heating in a microwave furnace, to improve the reactivity of the EAFS with the alkaline reagents. Different alkaline reagents with 99.8% purity and purchased from Sigma Aldrich (St. Louis, MO, USA), have been used, including KOH; K_2CO_3 ; KOH + K_2CO_3 ; NaOH; Na_2CO_3 ; and NaOH + Na_2CO_3 .

It is important to underline that preliminary experiments have shown that without conventional thermal or microwave treatment, co-grinding EAF/reagent mixtures did not allow any chemical reactivity likely to induce the formation of water leachable species containing metals (Cr, V) from the slag. Therefore, it is essential to implement either a thermal or a microwave pretreatment favoring the modification of the speciation of the targeted metals to obtain phases soluble in an aqueous medium. Some experiments carried out prior to this study involved the implementation of conventional thermal pretreatments [11]. The results obtained were conclusive regarding the leaching yields, but the treatment durations required to achieve the desired objective were too high. It therefore seemed necessary to

pretreat the slag/alkaline reagent mixtures under microwave radiation in order to reduce the treatment duration and consequently the expended energy. The co-grinded slag mixture and alkaline reagent was treated in microwave furnace according to the following method.

Heat Treatment and Activation Under Microwave Radiation

The tests were performed in a microwave furnace made by SAIREM company (Décines-Charpieu, France), allowing power modulation from 0.6 to 6 KWh. The sample temperature measurements in the microwave furnace were carried out using a portable infrared thermometer (AMPROBE, Everett, WA, USA, IR-750-EUR). As previously performed in the conventional heat treatment method [11], 2 g of the co-grinded mixture was introduced into an alumina crucible. Considering such treatment, quantities of activation energy depending on the microwave power and residence times have been studied. These treatments may induce the formation of species (chromates and vanadates), which are easily leachable in water. An important part of this work aims at optimizing the parameters and the operating conditions necessary for the recovery of metals (V and Cr) from the slag. The modified mixtures were then introduced in water for metal leaching at an S/L value of 40 g/L. After solid/liquid separation, the obtained filtrates were analyzed by AAS to allow for the calculation of the leaching rate and, consequently, to determine the effectiveness and potential selectiveness of each pathway treatment.

The experimental protocol includes two steps (Figure 1).

- Physical preparation of materials including crushing, magnetic separation, grinding, and, finally, co-grinding involving slag and alkaline reagents.
- Modification of metal speciation by microwave treatment and then leaching.

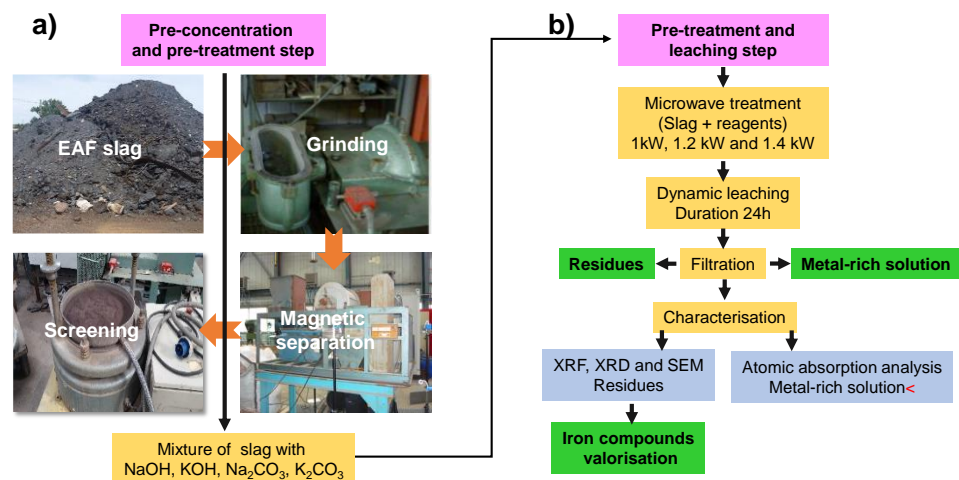


Figure 1. Experimental protocol for the recovery of Cr and V from EAFs. (a) physical treatment and (b) modification metal speciation.

3. Results

3.1. Physicochemical Characterization

An in-depth characterization of the microstructure of a few grains of the iron scrap-free slag by SEM clearly showed the great morphological variability of the grains, which should be correlated with their chemical heterogeneity [1]. The chemical analysis results of the investigated EAFS sample show that this slag contains 48.5% Fe, 29.5% Ca, 5.7% Si, 5.7% Mn, 5.2% Al, and 4.3% Mg, expressed, respectively, as Fe₂O₃, CaO, SiO₂, MnO, Al₂O₃, and MgO, and other elements, expressed as metals, such as Cr (3.4%), V (1450 ppm), and Mo (154 ppm) [1]. The XRD analysis of the investigated slag sample [1] revealed the following crystallized phases: larnite (Ca₂SiO₄), srebrodolskite (Ca₂Fe₂O₅), magnetite (Fe₃O₄), maghemite (Fe_{2.6}O₃), wustite (FeO), and magnesio-chromite (MgCr₂O₄), as reported in the literature [14–18]. Chromium-bearing compounds such as chromite were

detected, but this element is probably dispersed in various other mineral phases. The most common crystalline phases were srebrodolskite, wustite, magnetite, and probably magnesio-chromite. The EDS-SEM mapping (Figure 2) made it possible to establish a partial correlation between Cr and Mn concerning certain grains moderately loaded with Mn but heavily loaded with Cr. Furthermore, grains lightly loaded with Cr were present. This clearly indicates the presence, in the sample, of at least two types of Cr carriers. The particles lightly loaded with chromium appeared poor in iron. Conversely, the iron-rich particles do not contain chromium.

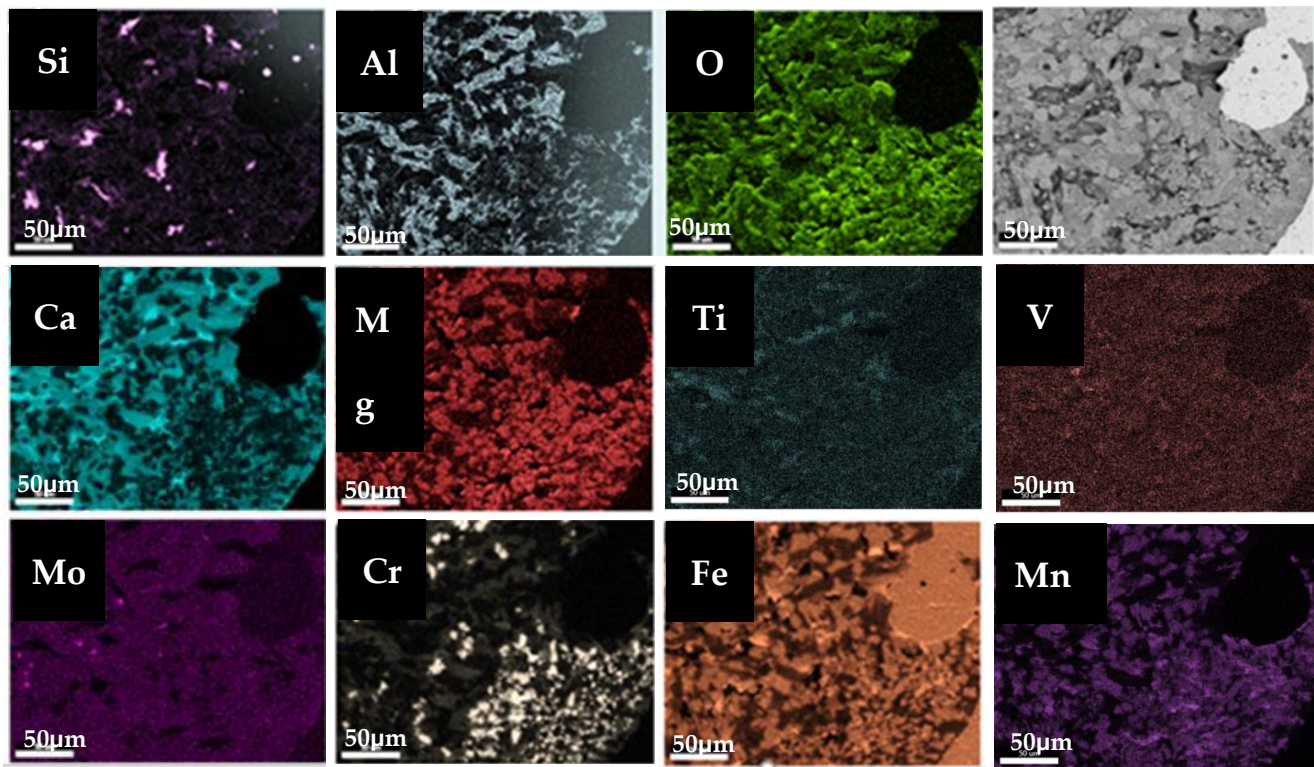


Figure 2. Mapping of different elements in EAFS by SEM-EDS.

Likewise, chromium rich particles contain, or not, little amount of iron. There is a correlation between calcium and aluminum, which most likely indicates the presence of larnite, which does not appear to contain chromium, as shown by the element mapping.

3.2. Thermodynamic Considerations

The thermodynamic calculations, necessary for establishing the phase diagrams, were carried out using the HSC software version 9 in previous work [11]. As mentioned, such diagrams are necessary to select the alkaline reagents and the temperatures allowing for high reactivity between the crystalline slag phases and reagents in order to form chromates and vanadates leachable in water solution. These diagrams clearly show that soluble chromates and vanadates of sodium or potassium can be obtained in a large range of oxygen and reagent partial pressures at different temperatures. Similar chemical behavior is expected to be exhibited under microwave radiation, which can also increase the slag/reagent mixture temperature. In such a context, this study deals with the recovery of Cr and V through the following method.

3.2.1. Leaching After Microwave Treatment

The EAFS/reagent mixture co-grounded for one hour was treated with microwaves at different powers and for residence times. After this, the EAFS/alkaline reagent mixture in deionized water was stirred and the obtained solutions were analyzed by AAS. Figure 3

shows the leaching rates of chromium (a) and vanadium (b) when the EAFS is treated using different alkaline reagents as dry (blue) and humid (red) mixtures for 15 min under 1.4 kW microwave power. Both the dry and humid mixtures exhibit similar reactivity even if leaching is a little higher when using humid mixtures, with the exception of NaOH. Consequently, most of this work has been performed by introducing small amounts of water (1 mL) into the mixtures to promote a temperature increase.

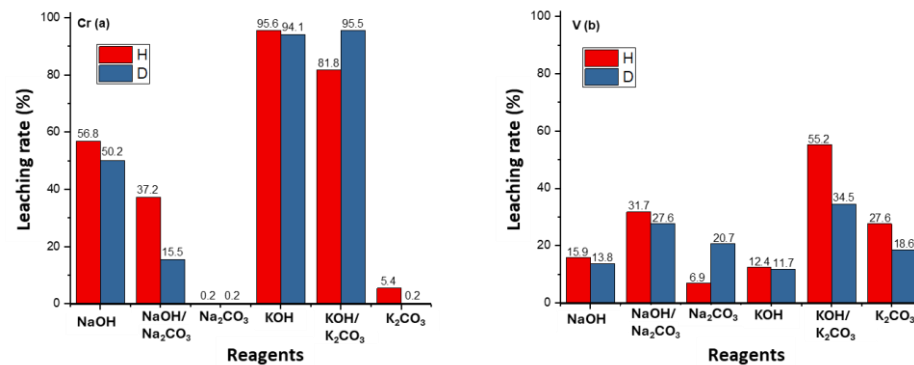


Figure 3. Leaching rates of Cr (a) and V (b) obtained using dry and humid methods through 1.4 kW microwave-assisted leaching for 15 min.

This figure clearly demonstrates that KOH-based reagents, whether used alone or in combination with K₂CO₃, are the most effective in promoting high chromium leaching from the EAF slag. This suggests that the chemical properties of these reagents play a significant role in enhancing the leaching process. In both configurations, wet and dry mixtures, KOH allows for more than 95% chromium leaching, while the mixture including KOH and K₂CO₃ allows for 95% (dry method) and 82% (wet method). Considering vanadium, through the dry and humid methods, the leaching rate is below 30%, except for the KOH + K₂CO₃ mixture, which allows for a leaching rate close to 35 and 55% considering, respectively, the dry and humid methods.

3.2.2. Effect of Microwave-Induced Temperature on Chromium Leaching

Figure 4 illustrates the results of different chromium leaching tests performed in a microwave furnace at 1.4 kWh for 15 min, inducing different temperatures for mixtures of alkaline reagents and EAF slag. The key trends observed from these tests highlight the impact of the temperature and reagent type on the efficiency of chromium extraction. Based on the results, the key findings are as follows.

1. EAF Slag with KOH: the highest chromium leaching efficiency is achieved at a roasting temperature of 670 °C.
2. EAF Slag with KOH + K₂CO₃: the optimal temperature for maximum chromium leaching is slightly lower, at 640 °C.
3. EAF Slag with Na₂CO₃ or K₂CO₃: the lowest leaching rate for each is obtained at the lowest roasting temperatures, respectively, 150 °C and 200 °C.

This suggests that the specific alkaline reagents used in the mixture, along with the precise control of the roasting temperatures, significantly impact the efficiency of the leaching process. The use of KOH alone requires a higher temperature, whereas the combination of KOH and K₂CO₃ lowers the optimal temperature needed for effective chromium recovery. These differences could be due to the varying reactivity and melting points of the alkaline reagents. These results depend also on how the reagents interact with the chromium in the EAFS during the MW treatment.

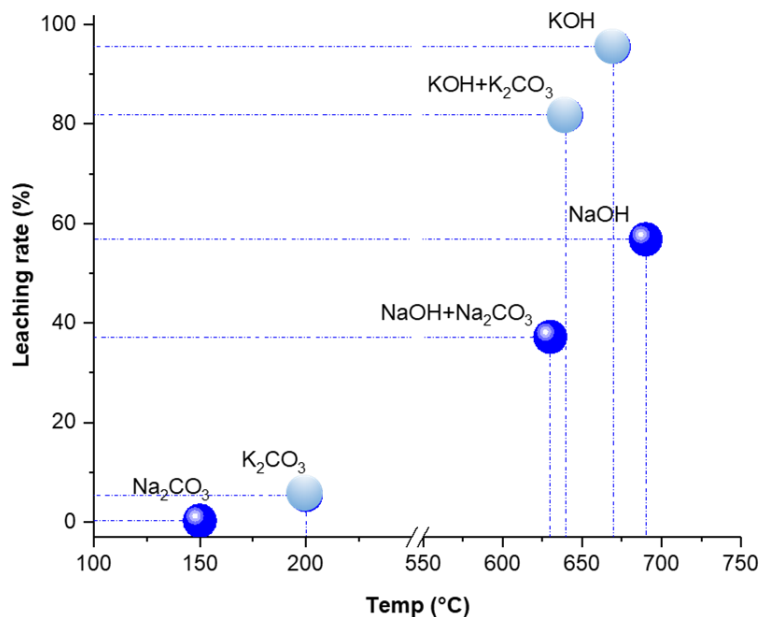


Figure 4. Leaching rates of Cr as function of MW (1.4 kWh)-induced temperature of different mixtures.

3.2.3. Effect of Microwave Power on Chromium and Vanadium Leaching

The left and right sides of Figure 5 show the leaching rates, respectively, of chromium and vanadium, for different microwave powers and different reagents, from the slag samples that were microwave-treated for 15 min. From this figure, it can be observed that when using KOH or KOH + K₂CO₃, chromium is dissolves more when increasing the MW power and is completely dissolved after 15 min under 1.4 kW of microwave power. However, when using NaOH or NaOH + Na₂CO₃ reagents, the leaching rates of chromium are close to, respectively, 60% and 20% at 1 kW, and these values are inverted when increasing the microwave power: the leaching rate increased up to 40% when using NaOH + Na₂CO₃ while it decreased close to 10% when using pure NaOH. This is likely due to the high reactivity of sodium carbonate with chromium upon increasing the microwave power, which promotes the formation of highly soluble chromate species in aqueous media. Potassium and sodium carbonates alone do not allow for the formation of great amounts of water-soluble chromium species no matter the microwave power used, as confirmed by the leaching rate of chromium being lower than 20%. This is probably due to the lower pH value induced by such reagents, which are less hard bases.

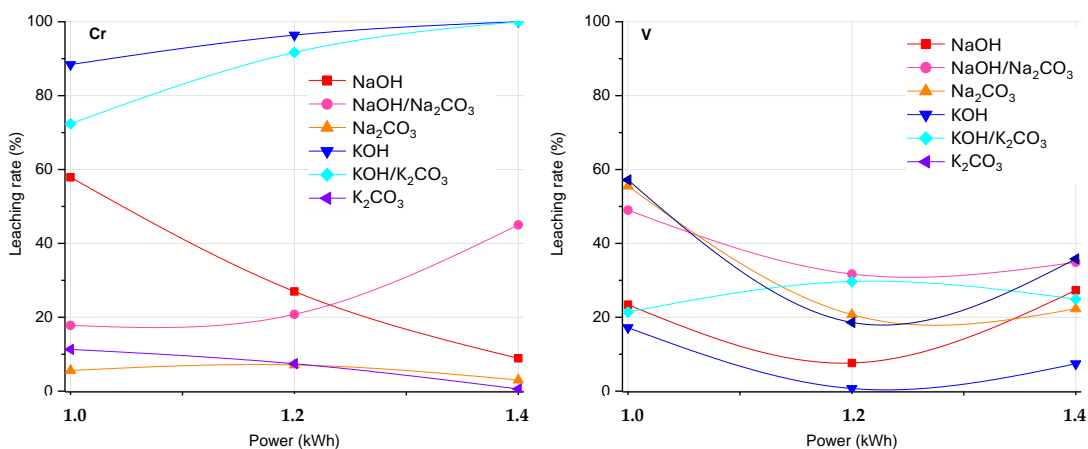


Figure 5. Leaching rates of Cr (left side) and V (right side) after slag treatment with the different alkaline reagents for 15 min using different microwave powers.

Considering vanadium, the highest leaching rates of 56 and 57% were obtained by treating the slag using, respectively, a Na_2CO_3 or K_2CO_3 mixture for 15 min with 1 kW of microwave power and these decreased when increasing the microwave power up to 1.4 kW (Figure 5, right). On the other hand, increasing the microwave power induces a decrease in vanadium leaching no matter the reagent, except for $\text{KOH} + \text{K}_2\text{CO}_3$. The reactivity of vanadium seems to be quite different to that of chromium when using KOH or $\text{KOH} + \text{K}_2\text{CO}_3$ reagents, which induce a lower leaching rate of vanadium (lower than 30%) compared to chromium (more than 70%; see Figure 5, left side).

3.2.4. Effect of Microwave Residence Time on Chromium and Vanadium Leaching

Figure 6 shows the evolution of the leaching rate of chromium (left side) and vanadium (right side) as a function of the residence time of different slag/alkaline reagent mixtures treated at 1.4 kW.

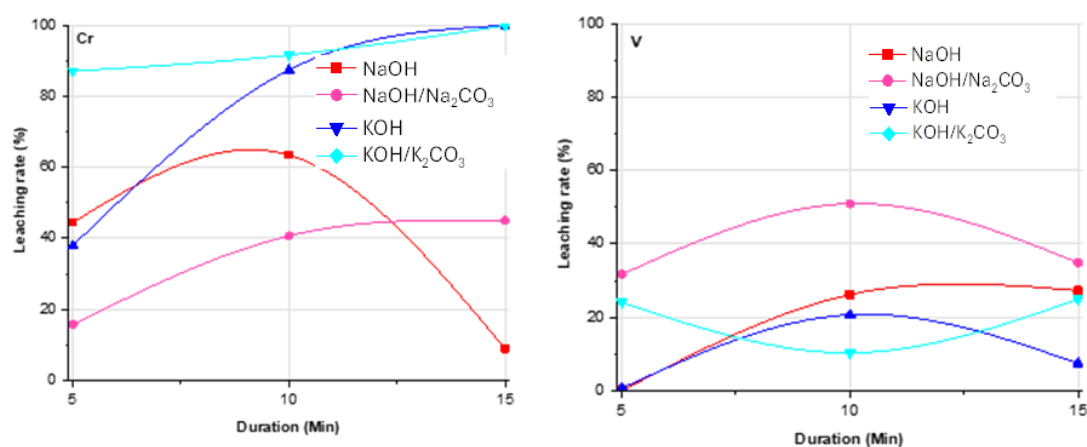


Figure 6. Leaching rates of Cr (left side) and V (right side) after slag treatment by most reactive alkaline reagents under 1.4 kW microwave power for different residence times.

The leaching rate of chromium increases from 38% to 100% in the case of using only KOH in the mixture. When using $\text{KOH} + \text{K}_2\text{CO}_3$, the leaching rate is very high (87%) after only 5 min of MW treatment. Then, the increase in the leaching rate up to 100% is slow when the residence time increases up to 15 min. This is due to K_2CO_3 's high reactivity with chromium species, which facilitates the formation of very soluble chromate species in water.

Considering the results of the vanadium leaching, shown on the right side of Figure 6, it is clear that vanadium-bearing minerals are less reactive with alkaline reagents than chromium-bearing ones. Indeed, whatever the reagent, the leaching rate of vanadium is less than 50%.

Therefore, considering the preparation of slag/alkaline reagent mixtures using microwaves, the optimal parameters to promote the leaching of valuable metals (Cr and V) are as follows.

1. Slag/ KOH or $\text{KOH} + \text{K}_2\text{CO}_3 = 1$, power = 1.4 kW, residence time = 15 min, $V_{\text{H}_2\text{O}} = 1$ mL to leach 100% Cr.
2. Slag/ K_2CO_3 or $\text{Na}_2\text{CO}_3 = 1$, $P = 1$ kW, residence time = 15 min, $V_{\text{H}_2\text{O}} = 1$ mL to leach more than 55% V.

Table 1 groups together the best leaching rates of V and Cr from EAFS obtained for the two conditions of conventional and microwave treatments. It can be seen that the conventional roasting method allowed the obtainment of a maximum leaching rate of 97.5% for Cr after one hour of co-grinding the mixture of EAFS/ $\text{NaOH} + \text{Na}_2\text{CO}_3$, and then two hours of conventional roasting at 800 °C. A leaching rate of 62.5% was obtained for V after three hours of co-grinding the slag/ $\text{NaOH} + \text{Na}_2\text{CO}_3$ mixture followed by two hours

of conventional roasting at 600 °C. On the other hand, after only 15 min of treatment under microwave conditions, the leaching rates of chromium and Vanadium are, respectively, 100% and 55%. Such results demonstrate the great benefit of using microwaves to optimize the modification of metal speciation to be leached. Consequently, the microwave-assisted leaching process optimized in this study can be considered an economical solution with less impact on the environment compared to the conventional leaching method.

Table 1. Best results obtained from leaching after conventional or MW furnace treatment.

Parameters	Microwave Roasting		Conventional Roasting	
	Cr	V	Cr	V
Reagents	KOH KOH + K ₂ CO ₃	Na ₂ CO ₃ K ₂ CO ₃	NaOH + Na ₂ CO ₃	NaOH + Na ₂ CO ₃
Co-grinding residence time	1 h	1 h	1 h	3 h
Temperature (power)	900 °C (1.4 kW)	500 °C (1.0 kW)	800 °C	600 °C
Residence time	15 min	15 min	2 h	2 h
Leaching rate	100%	56–57%	98%	63%

At the end of the leaching experiments, the Eh and pH values of the leachates were measured. Figure 7 brings together the Eh-pH diagrams of the following systems: Cr-Na-H₂O, V-Na-H₂O, Cr-K-H₂O, and V-K-H₂O at 25 °C.

At the end of the experiments, the pH values were around 13 for all the leaching solutions. However, the redox potential (Eh) values were between 0.2 and 0.3 V/NHE in the sodium medium and between 0.3 and 0.4 V/NHE in the potassium medium. In such Eh-pH conditions (shown by the red star on the graph in Figure 7 and in the presence of KOH or NaOH, the Eh-pH diagrams show that chromium is in the form of chromate anions, CrO₄²⁻. Such thermodynamic results for chromium speciation seem to be in perfect agreement with the experimental results obtained when KOH is used. Indeed, during the experiments, the concentration of chromium reached the maximum when using KOH and the microwave treatment. When using NaOH, the solubility of chromium is lower than 50% no matter the duration, probably due to the low reaction kinetics. These results indicate a lower reactivity of chromium bearing-minerals with such reagents. On the other hand, when potassium hydroxide is used as an alkaline reagent, VO₄³⁻ anions are supposed to be formed, as shown by the diagram in Figure 7. Yet, the leaching rate of this metal is lower than 20%.

Considering reagents including sodium hydroxide for the leaching of vanadium, taking into account the measured Eh/pH values, sodium vanadates Na₂V₂O₇ should be formed, which are very water-soluble phases. This explains the higher rate of V leaching when using NaOH than that when using reagents containing KOH.

It is important to notice that chromium leaching is strongly dependent on acid-base and redox conditions. The study by Bäverman et al. [19] highlighted the difficulty of establishing similarities between simulation and experimentation for this metal. It is also possible that the variety of aqueous complexes considered by the authors is insufficient to calculate correctly the speciation of chemical compounds in solution under pH or redox conditions, which can evolve significantly. Therefore, considering the solubility of chromium and vanadium species, the evaluation of saturation indices can be distorted as the system evolves.

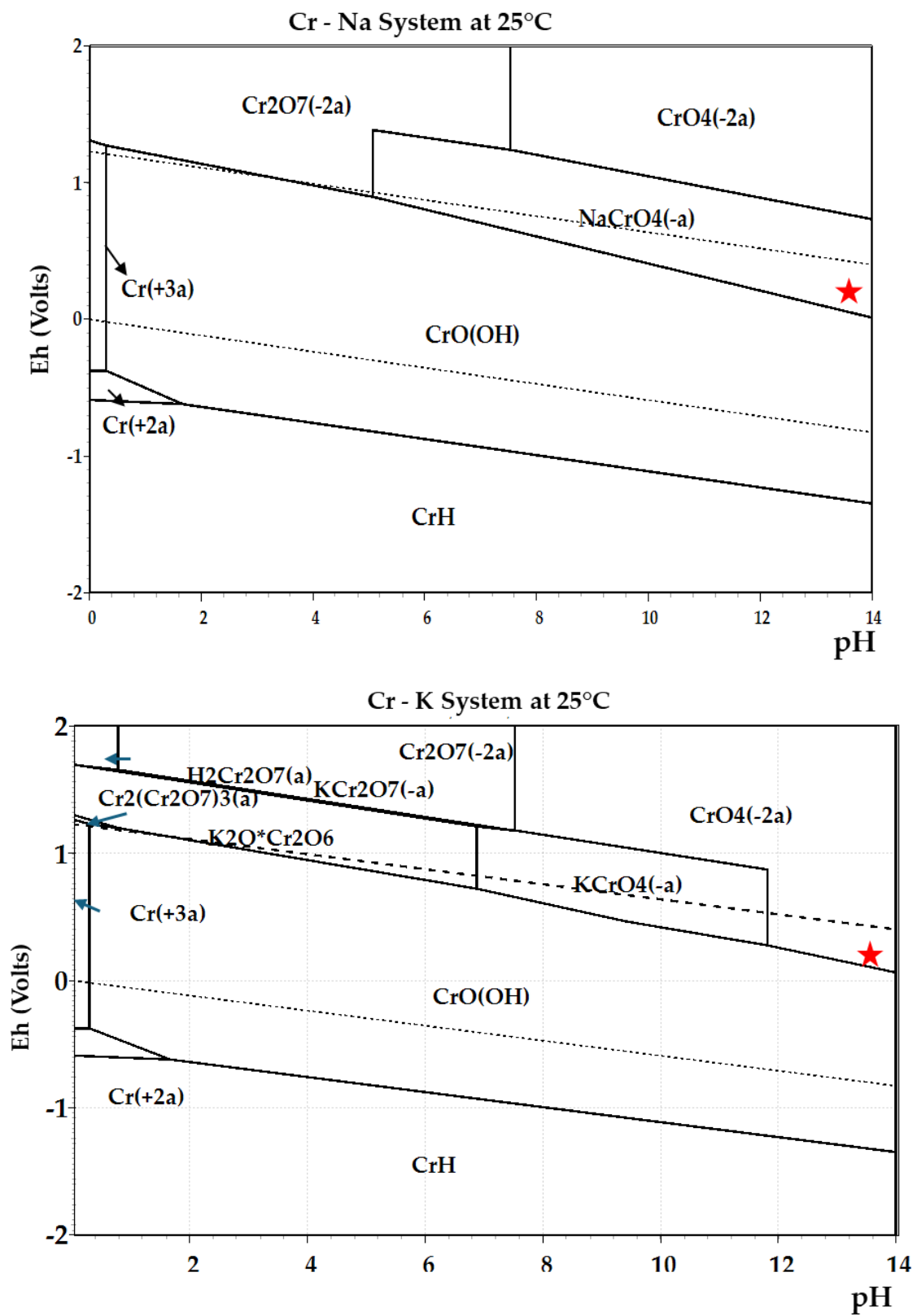


Figure 7. Cont.

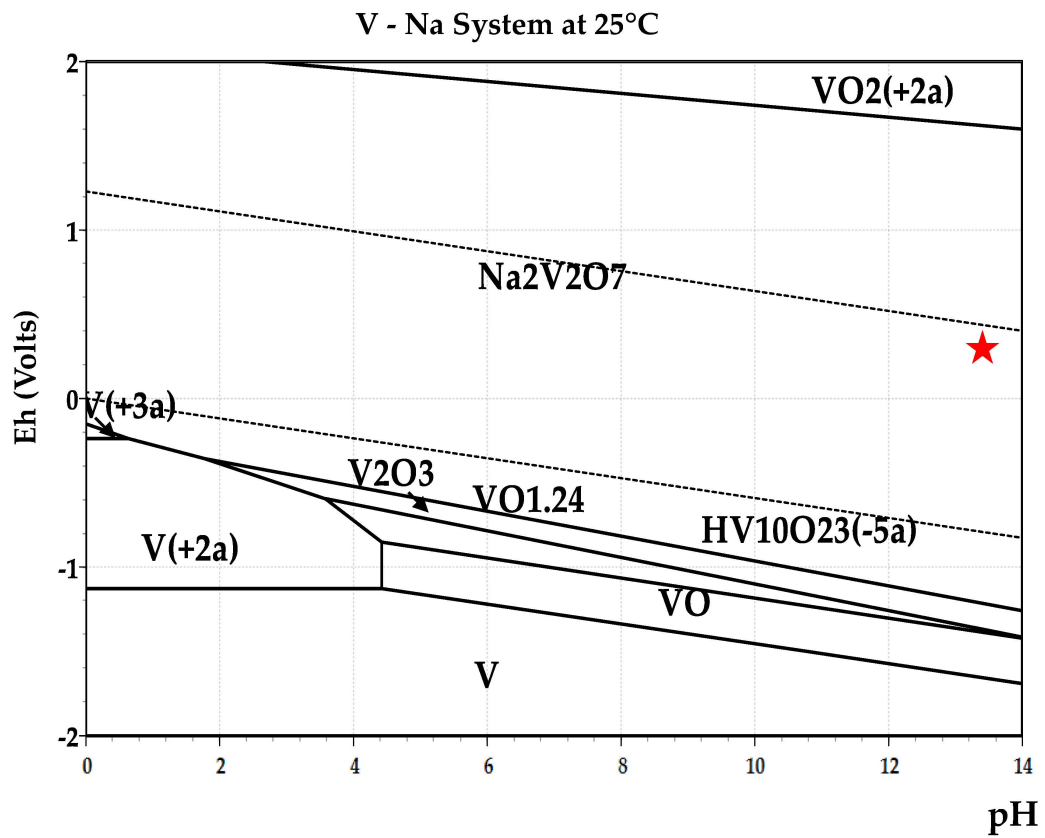
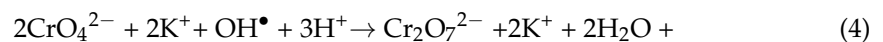
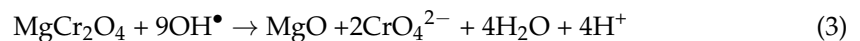


Figure 7. Eh-pH diagrams of Cr-Na-H₂O, V-Na-H₂O, V-K-H₂O, and Cr-K-H₂O systems at 25 °C.

Considering chromium species, the reaction pathway during MW treatment is expected to be as described in reaction (1). As shown by the phase diagrams of the O-Cr-K and O-Cr-Na systems at 400 and 600 °C (Figure 3), chromate species could be directly obtained by the reaction of chromite with potassium hydroxide.

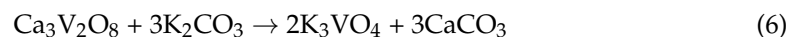
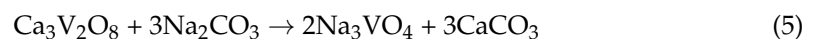


But the chemical reaction mechanism is probably more complex; this is due to the potential formation of OH^\bullet free radicals (reaction (2)). These radicals, which mainly come from radiation–matter interactions, are considered major chemical species able to react with phases within slag due to their single electron on the peripheral layer, which gives them a high reactivity. It can be hypothesized that the reaction mechanism is consequently identical to that of reaction (3), where the hydroxyl radical OH^\bullet reacts as a strong oxidant ($\text{OH}^\bullet/\text{H}_2\text{O}$: 2.34 V/ENH) with respect to chromite ore, which could be present in the form of FeCr_2O_4 in our slag sample. Chromates are obtained according to reaction (3) and then could be oxidized into dichromate according to reaction (4).



Similar mechanisms are expected concerning the reactivity of slag minerals with other alkaline reagents (NaOH , Na_2CO_3 , K_2CO_3 , or mixtures), inducing the formation of leachable species such as chromates and vanadates in aqueous media. However, the results obtained with these other reagents are less efficient and therefore seem to indicate significantly different reaction patterns or reaction kinetics.

Considering vanadium, the best reactivities were observed when using K_2CO_3 under microwave radiation or $\text{NaOH} + \text{Na}_2\text{CO}_3$ using conventional heat treatment. This can be explained through Equations (5) and (6), which highlight the formation of soluble sodium and potassium vanadates.



4. Conclusions

Steel slag (SS) represents a promising secondary resource due to its high critical metal content, such as that of chromium (Cr) and vanadium (V). This study was conducted with the aim of developing a methodology to recover chromium and vanadium from EAF slags by using alkaline reagents. The slag characterization showed that the main crystalline phases contained in this heterogeneous material were srebrodolskite, larnite, hematite, and others, some of these minerals being expected to be Cr or V carriers. To explore this two-element leaching, an innovative technique was carried out involving physical preparation by co-grinding slag with alkaline reagents and then treatment in microwave furnaces to modify the metal speciation and consequently generate water-soluble species. Such a process allows for the leaching of a high proportion of metals, particularly chromium and vanadium. The leaching rate of chromium and vanadium were, respectively, 98% and 63% after 2 h of conventional heat treatment while MW treatment allowed for leaching close to 100% and 56–57% of the chromium and vanadium, respectively, after only 15 min of treatment in a microwave furnace. This study clearly justifies the great interest in metal-bearing species modification by microwave treatments, which allow for the enhancement of reaction kinetics and consequently have a lower energy demand.

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